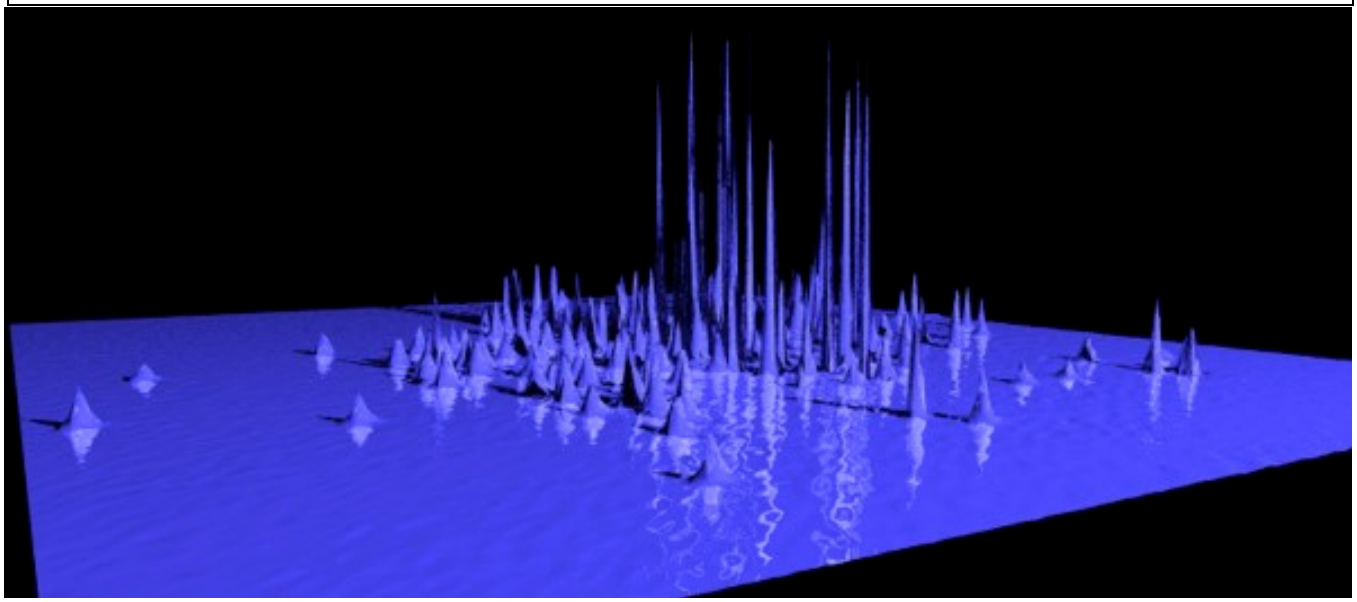
NMR SPECTROSCOPY



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SECTION 1 – ^{1}H NMR

Why compounds absorb radiowaves (background information beyond specifications)

- NMR (nuclear magnetic resonance) is a very powerful tool for identifying compounds.
- The nucleus of some atoms has nuclear spin (e.g. ^{1}H, ^{13}C, ^{19}F, ^{31}P), although many atoms do not have any nuclear spin (e.g. ^{12}C).
- A nucleus with spin generates a small magnetic field.
- When a nucleus with spin is placed in a magnetic field, the small magnetic field generated by the nuclear spin can be aligned with or against the main magnetic field.
- There is a small difference in energy between these two alignments that corresponds to the energy of radiowaves. Consequently, if radiowaves are passed through the substance, some frequencies of radiowaves will be absorbed to flip the nucleus from one spin direction to the other.
- The resulting spectrum gives valuable information about the compound.
- NMR is especially useful to organic chemists as they can find out about the H atoms (through ^{1}H NMR) and the C atoms (through ^{13}C NMR)
- NMR has many uses in medicine and MRI (magnetic resonance imaging) machines are a type of NMR machine.

How NMR is done

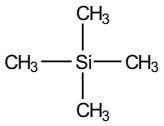
- The sample is usually dissolved in a solvent in a long thin tube and placed inside the machine where it is bombarded with radiowaves in a strong magnetic field. (the stronger the magnetic field the better the resolution of the signals)

Solvents

- If the solvent contains any ^{1}H atoms, then these will appear in the spectrum (and may hide signals due to H atoms in the sample).
- Consequently solvents are used that contain no ^{1}H atoms. Often these solvent contain deuterium (D or ^{2}H) atoms instead of ^{1}H atoms as D atoms have no nuclear spin.
- Examples of commonly used solvent include: CCl_4 and deuterated solvents such as $CDCl_3$, C_6D_6, etc.

Calibration

- To calibrate the spectrum, a small quantity of tetramethylsilane (TMS) is added to samples as this produces a signal providing an internal standard to which other peaks are compared.



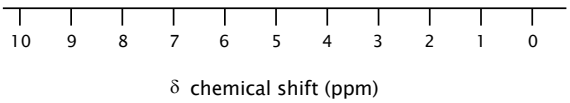
- This is used because:
  - it only gives one signal,
  - it is non-toxic,
  - it is inert,
  - it has a low boiling point (26°C) and so can be easily removed from the sample afterwards,
  - it gives a signal that is further right than most of the signals from organic compounds.

Chemical shift

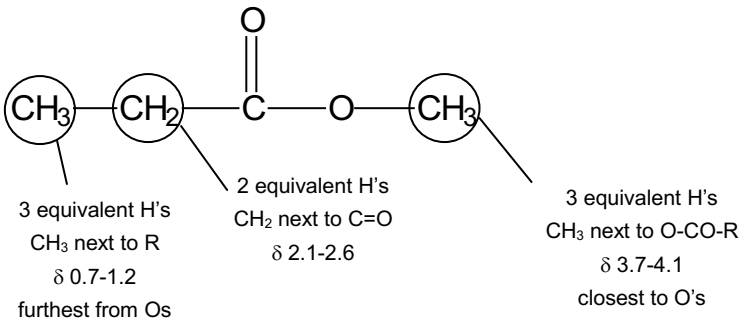
- The spectra are recorded on a scale known as the chemical shift (δ), which is how far the signal is away from the signal for TMS is parts per million.

$$\delta = \frac{\text{Field for TMS - Field measured}}{\text{Field for TMS}} \times 10^6$$

- Most signals are between 0 and 10 ppm away from the signal for TMS, and the scale is usually shown as below on the final spectrum.



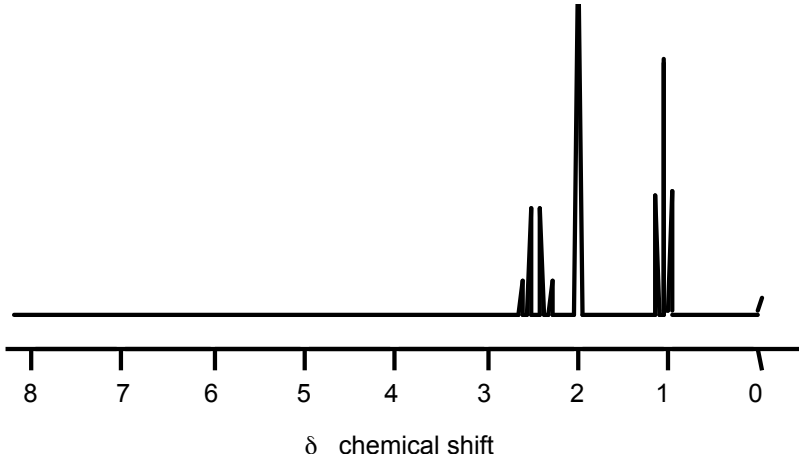
- The chemical shift depends on what other atoms/groups are near the H. The closer the H is to electronegative atoms (e.g. O, Cl), the greater the shift. Also the more electronegative atoms near, the greater the shift. In the example below, it can be seen that the closer the Hs to any O's, the greater the chemical shift.



- The data sheet can be used to find approximate values for chemical shifts. It is not always straightforward using the limited data in this table, but the best match is taken. The example above shows how this can be done.

What a spectrum looks like

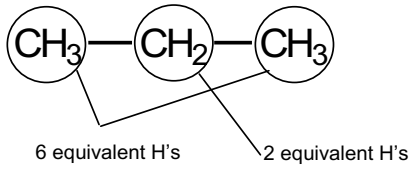
- The data is analysed by a computer and a spectrum produced.



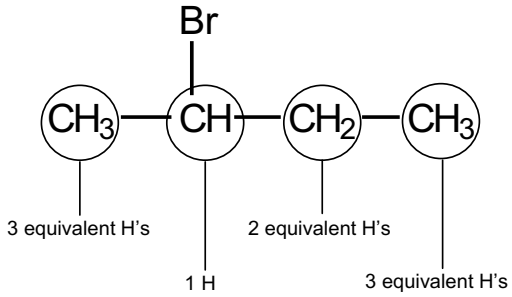
- The spectrum contains a series of signals (or peaks) showing where the compound absorbs radiowaves.
- The horizontal scale is the chemical shift (δ) – this indicates how far each signal is shifted away from that for TMS (measured in parts per million).
- The vertical axis represents the intensity of the absorption.

Number of signals - equivalent H atoms

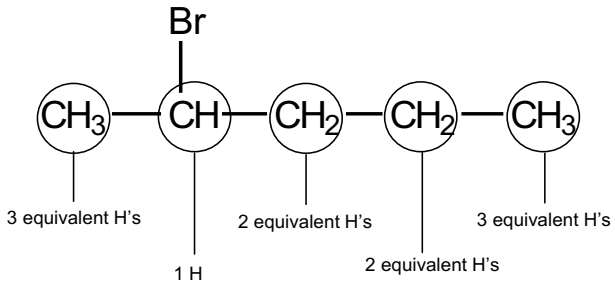
- In a spectrum, there is one signal for each set of equivalent H atoms, with the area of each signal being proportional to the number of equivalent H atoms it represents.
- Here are some examples.



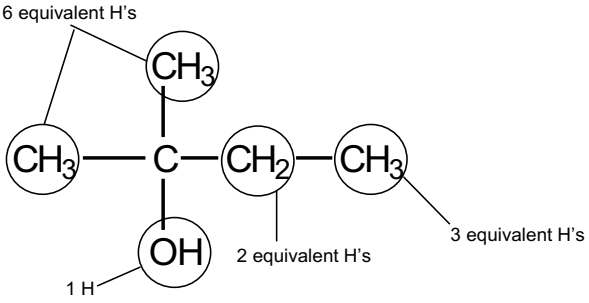
2 signals



4 signals



5 signals



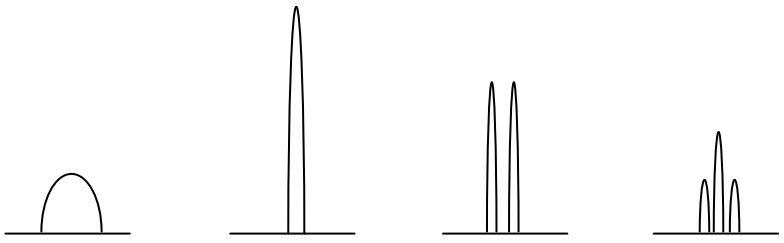
4 signals

TASK 1a – Predicting the number and intensity of signals

In TASK 1 on page 9, draw the structure of each compound and then predict the number and relative intensity of the signals.

Relative intensity of signals – number of equivalent H atoms

- In ^{1}H NMR (but **not** ^{13}C NMR) the area of the signal is proportional to the number of H atoms it represents.
- It is not the height of the signal that matters but the overall area that the signal covers. For example, the following four signals have the same area and so represent the same number of H atoms, even though they have different heights and in some cases are made of a number of individual peaks



There are four signals here – each has the same area and so represents the same number of H atoms

- There are a number of ways in which the relative size (area) of the signals can be shown. The most common one at A level is to indicate the relative intensity of the signals from which the simplest whole number ratio can be calculated.

e.g. relative intensity = 1.2 : 1.2 : 1.8 = 2 : 2 : 3

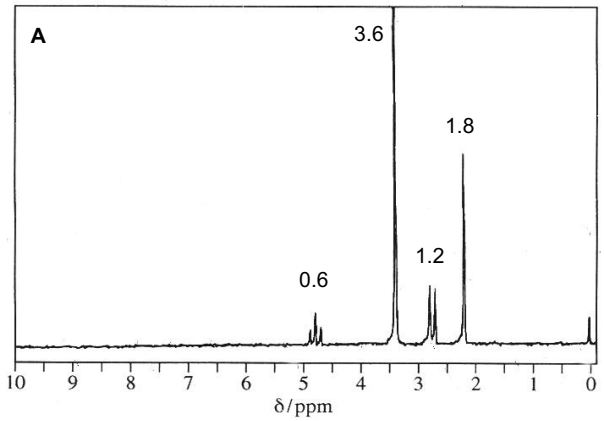
relative intensity = 2.1 : 2.8 = 3 : 4

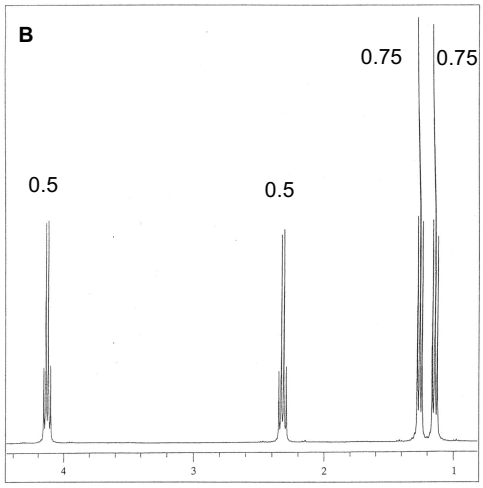
relative intensity = 1.5 : 0.5 : 2.0 = 3 : 1 : 4

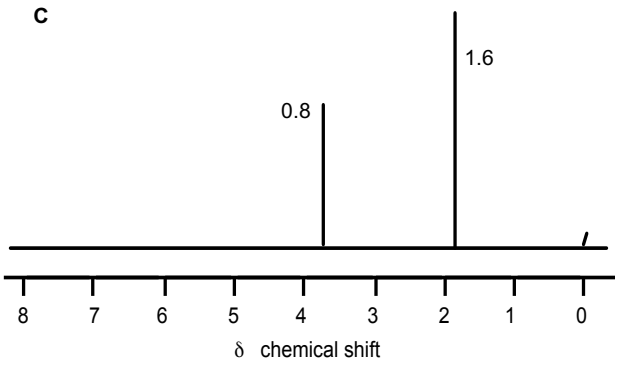
relative intensity = 0.3 : 0.15 : 0.3 : 0.6 = 2 : 1 : 2 : 4

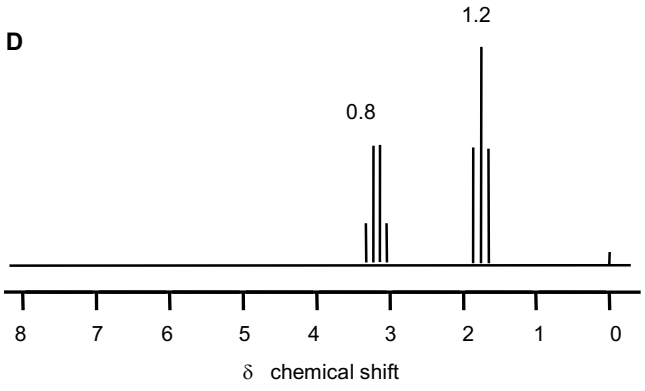
TASK 2 – Finding the relative intensity of signals from a spectrum

For each of the NMR spectra below, calculate the relative number of H atoms associated with each signal.



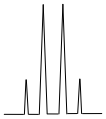






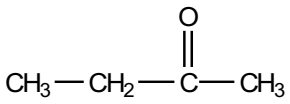
Splitting patterns (also known as coupling or multiplicity)

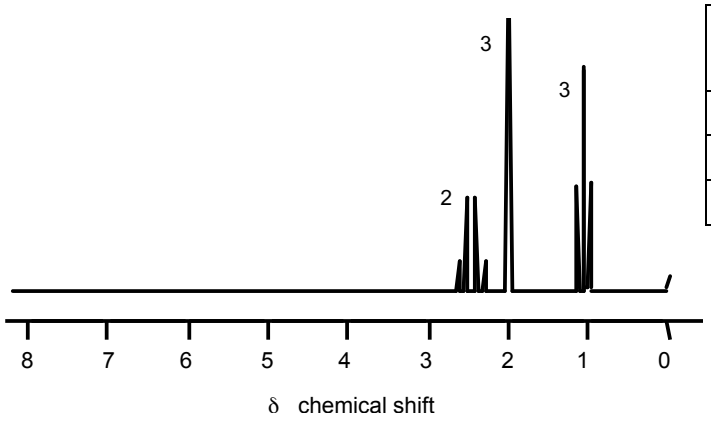
- The number of lines a signal is split into gives information about neighbouring H atoms - whether they are inequivalent, and if they are, how many H atoms there are.
- Usually only H atoms on the neighbouring C atom cause splitting (coupling).
- The signal for H atoms is only split by inequivalent Hs – so if the H atoms on the next atom are equivalent they do not cause splitting.
- **The number of lines = 1 + the number of inequivalent H atoms on adjacent C atoms** (the "n+1" rule)
- If there are more than 3 neighbouring inequivalent H atoms, then it can be classed as a multiplet (though exam questions are unlikely to involve these).

signal	singlet (s)	doublet (d)	triplet (t)	quartet (q)
appearance				
number of lines	1	2	3	4
number of neighbouring inequivalent H atoms	0	1	2	3
relative size		1:1	1:2:1	1:3:3:1

- It should be noted that the H atom of the OH group in alcohols rarely causes splitting (couplings), or is split (coupled) itself. Sometimes the H atom of an OH group appears as a broad hump.

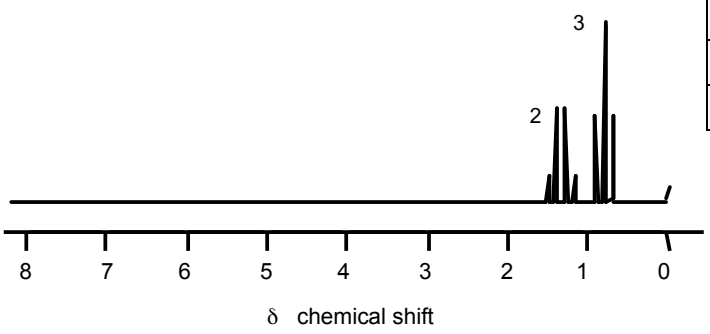
Example 1 - butanone





shift (δ)	assignment	relative intensity	coupling	coupled to
1.0	$C\underline{H}_3CH_2$	3	triplet	CH_2
2.0	CH_3CO	3	singlet	
2.4	CH_2	2	quartet	CH_3

Example 2 - butane

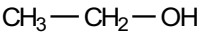


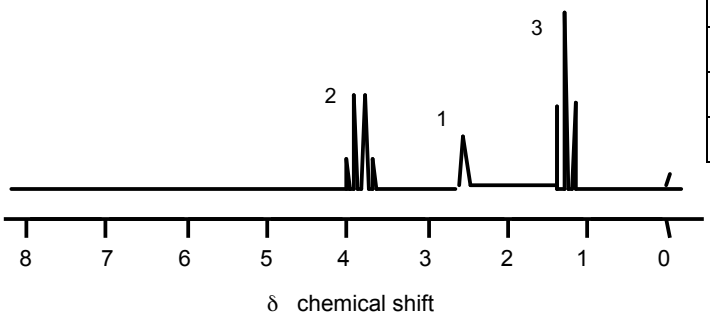
shift (δ)	assignment	relative intensity	coupling	coupled to
1.3	CH_2	2	quartet	CH_3
0.8	CH_3	3	triplet	CH_2

Note:

The CH_2 only couples to the CH_3 and not the other CH_2 as the CH_2 is equivalent.

Example 3 - ethanol





shift (δ)	assignment	relative intensity	coupling	coupled to
1.3	CH_3	3	triplet	CH_2
2.6	OH	1	singlet	
3.8	CH_2	2	quartet	CH_3

Note:

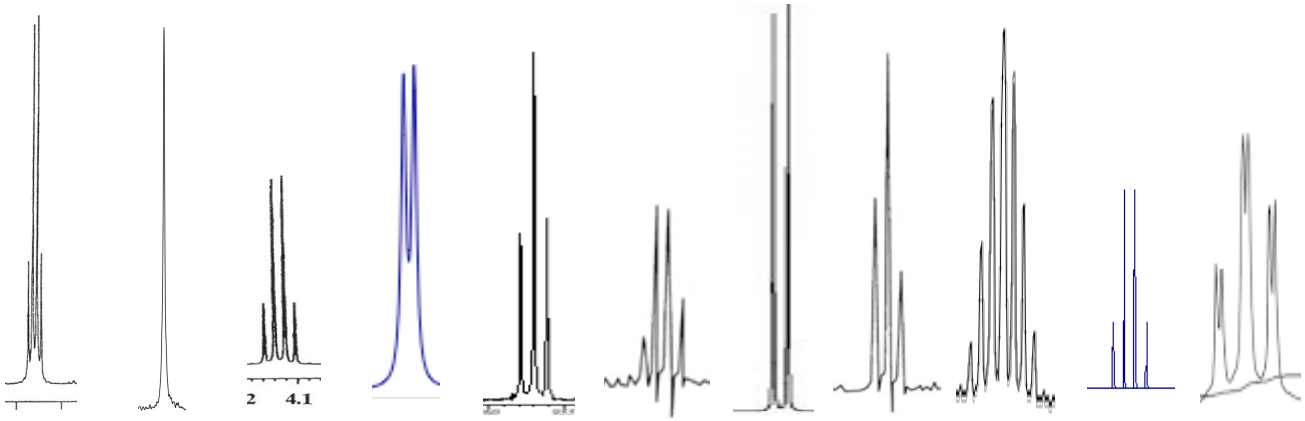
The CH_2 and OH do not couple to each other (alcohol OHs rarely get involved in coupling)

TASK 1b – Predicting splitting patterns

In TASK 1 on page 9, predict the splitting pattern of each signal.

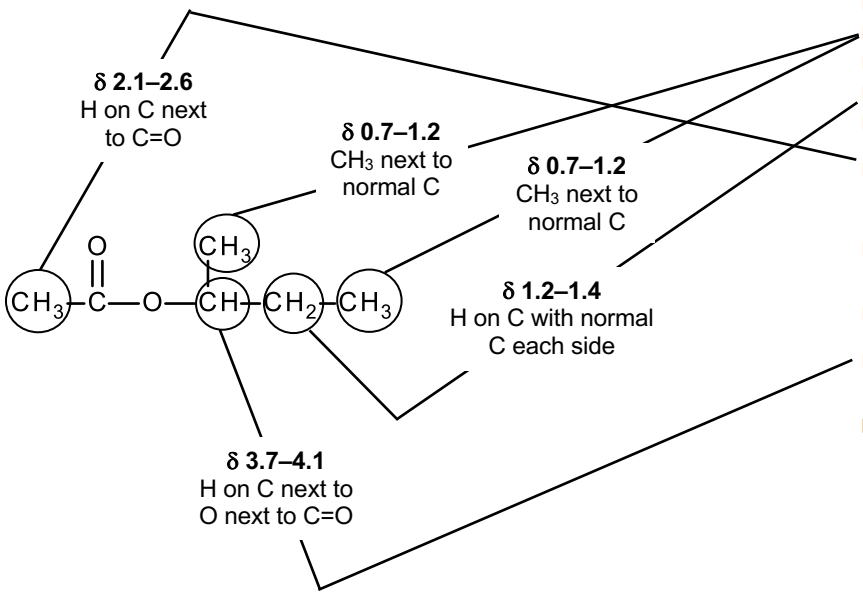
TASK 3 – Identifying splitting patterns

Look at each of the following signals and decide whether it is a singlet (s), doublet (d), triplet (t), quartet (q) or multiplet (m).



The position of signals

- The chemical shift (δ) of each signal gives us information about the chemical environment of the H atoms in the molecule.
- The closer the H atoms are to very electronegative atoms (e.g. O, Cl) and/or double bonds, the greater the chemical shift.
- Table of data can give us guidance as to what the chemical shift will be. Often, the exact environment of the H atom will not be in the data table, but we should look for the closest match.
- An example is shown below:

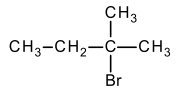


Type of proton	δ/ppm
ROH	0.5 – 5.0
RCH_3	0.7 – 1.2
RNH_2	1.0 – 4.5
R_2CH_2	1.2 – 1.4
R_3CH	1.4 – 1.6
R–C(=O)–C(H)–	2.1 – 2.6
R–O–C(H)–	3.1 – 3.9
RCH_2Cl or Br	3.1 – 4.2
R–C(=O)–O–C(H)–	3.7 – 4.1
R(H)C=C(H)	4.5 – 6.0
R–C(=O)H	9.0 – 10.0
R–C(=O)–O–H	10.0 – 12.0

TASK 1c – Predicting chemical shifts

In TASK 1 on page 9, predict the chemical shift of each signal.

TASK 1 – Predicting ^{1}H NMR spectra

Compound	Structure	Number of signals	Relative intensity of signals	Splitting patterns of signals	Position of signals
2-bromo-2-methylbutane		3	3 : 2 : 6	t, q, s	δ 0.7-1.2 (3, t) δ 1.2-1.4 (2, q) δ 0.7-1.2 (6, s)
methylpropene					
propene					
2-chloropropane					
propanone					
methylamine					
ethyl propanoate					
1,2-dibromopropane					
dimethylethyl propanoate					
but-2-ene					

TASK 4 – Predicting ^{1}H NMR spectra

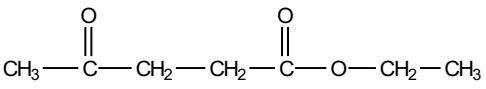
Compound	Structure	Number of signals	Relative intensity of signals	Splitting patterns of signals	Position of signals
2,3-dimethylbutane					
3,4-dimethylheptane					
cyclohexane					
methylcyclohexane					
2-bromo-3-chlorobutane					
pentan-3-one					
2-methylpropan-2-ol					
propanoic acid					
methyl propanoate					
methylpropanal					

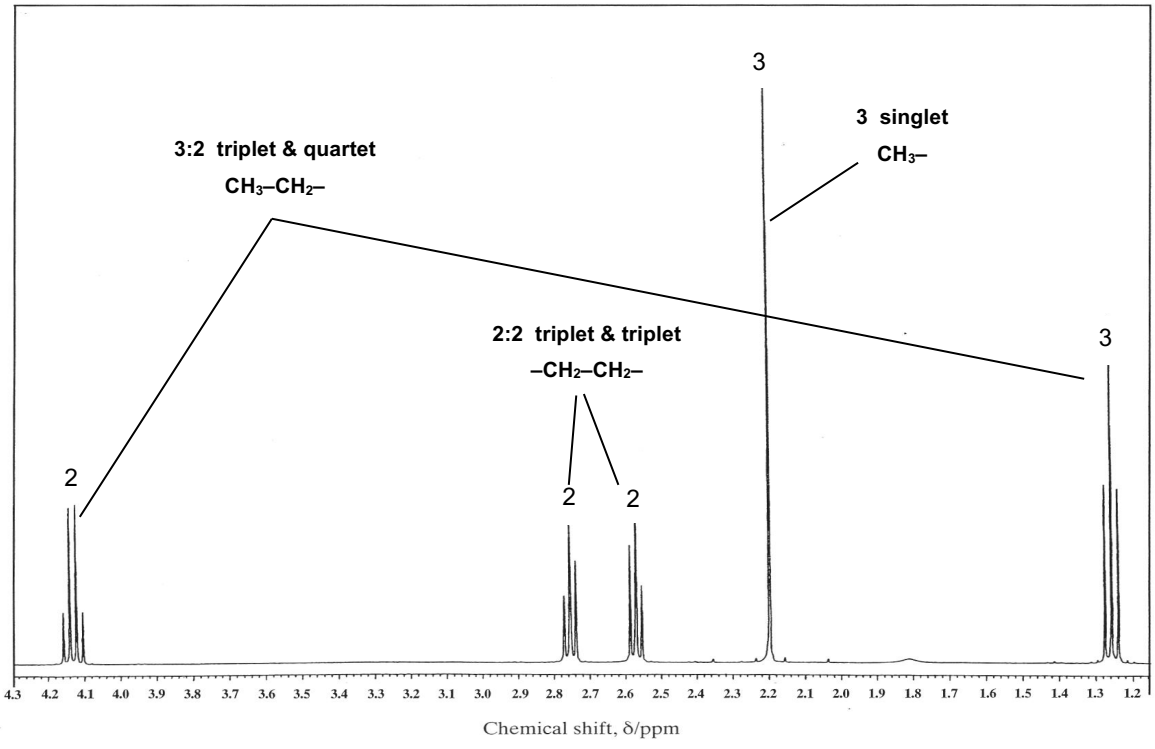
Some common signals to look out:

The following patterns crop up over and over again and it is very handy if you can spot them as you work towards working out the structure of a molecule.

Triplet & quartet	3:2	$CH_3–CH_2–$ (ethyl group)	• The triplet and quartet do not have to be next to each other in the spectrum. • The atom joined to the other side of the CH_2 cannot have any H's on (unless they do not do not couple, e.g. OH group or an equivalent CH_2 as in butane).
Triplet & triplet	2:2	$–CH_2–CH_2–$	• The two triplets do not have to be next to each other in the spectrum. • The two CH_2 groups must be inequivalent (otherwise they would produce one signal not two!). • The atoms joined either side of the CH_2s cannot have any H's on them.
Doublet & quartet	3:1	$CH_3–CH–$	• Doublet and quartet do not have to be next to each other in the spectrum. • The atom joined to the other side of the CH cannot have any H's on (unless they do not do not couple, e.g. OH group or an equivalent CH).
Singlet	3	$CH_3–$ (methyl group)	• The atom joined to the CH_3 cannot have any H's on it.
Singlet	1	–OH	• A singlet for 1H is usually an OH on either an alcohol or a carboxylic acid. • This H does not usually couple to other H atoms, even if there is an H on the next C atom, and so is a singlet and any Hs on the next C atom are not split by the H of the OH.

This example spectrum contains three of these signals. The spectrum is of this compound:





TASK 5 – Which ^{1}H NMR spectrum is which?

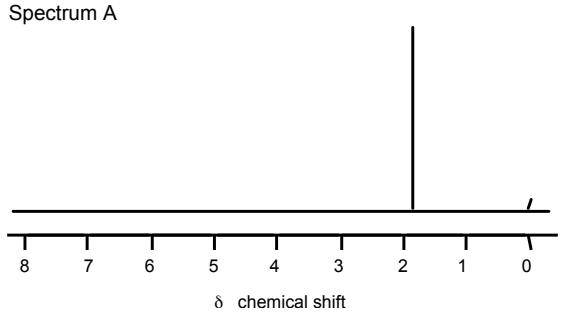
For each of the following compounds:

CH_3CH_2I $(CH_3)_3CBr$ CH_3COCH_2OH $(CH_3)_3COH$ $CH_2ClCHCl_2$ $(CH_2Br)_2CBrCH_3$ $(CH_3)_2CBrCH_2Br$

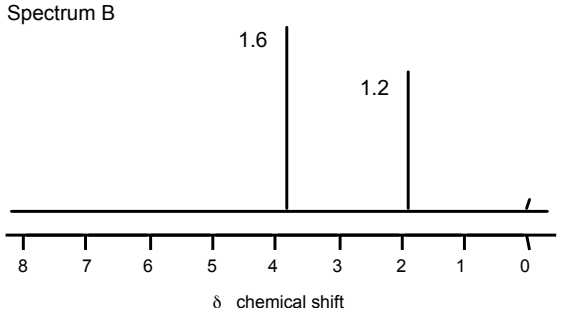
a) For each compound, predict the number of signals, and relative intensity and multiplicity of each signal.

b) Work out which spectrum belongs to which compound.

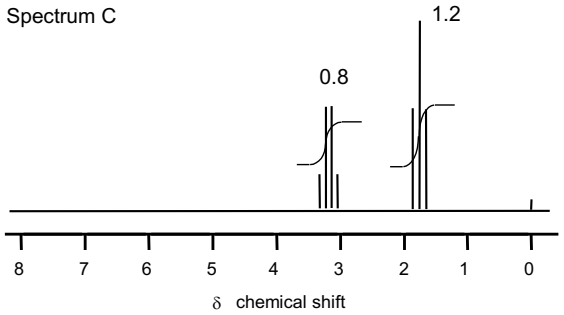
Spectrum A



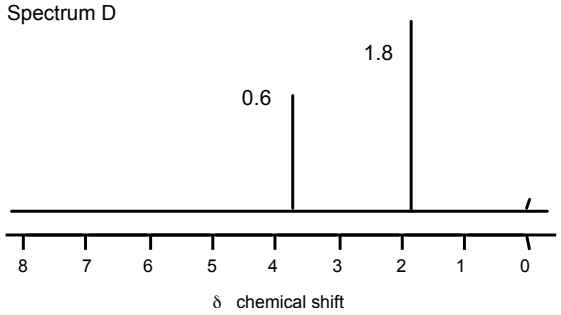
Spectrum B



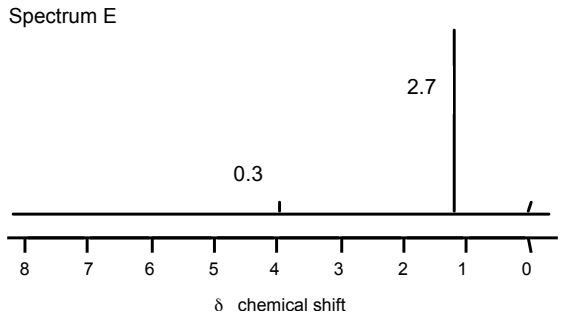
Spectrum C



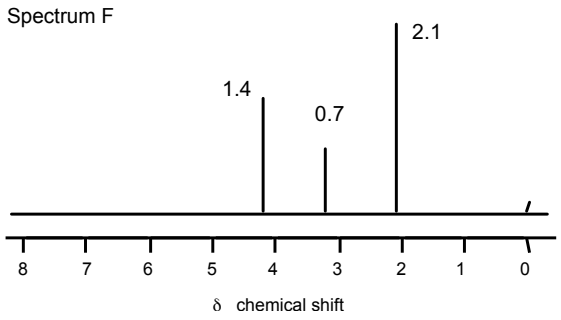
Spectrum D



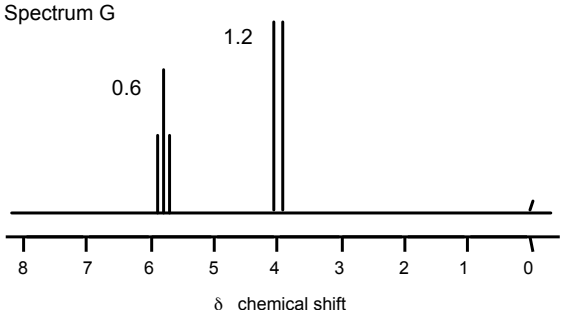
Spectrum E



Spectrum F



Spectrum G



TASK 6 – Identifying compounds

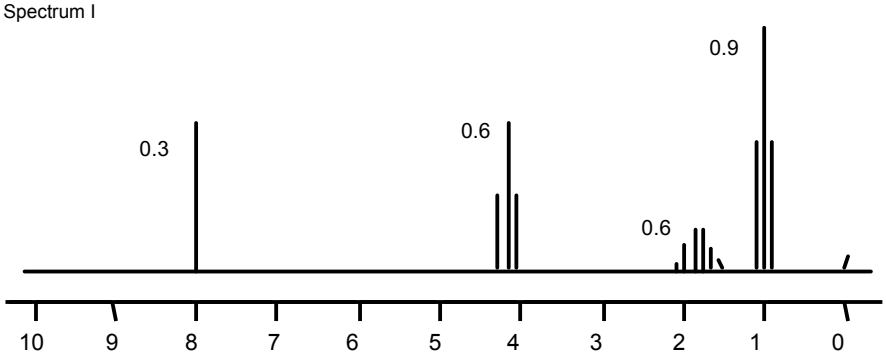
The ^1H NMR spectra of three isomers of $C_4H_8O_2$ are shown.

a) Draw the structural formulae of all the isomers of $C_4H_8O_2$ that are carboxylic acids or esters.

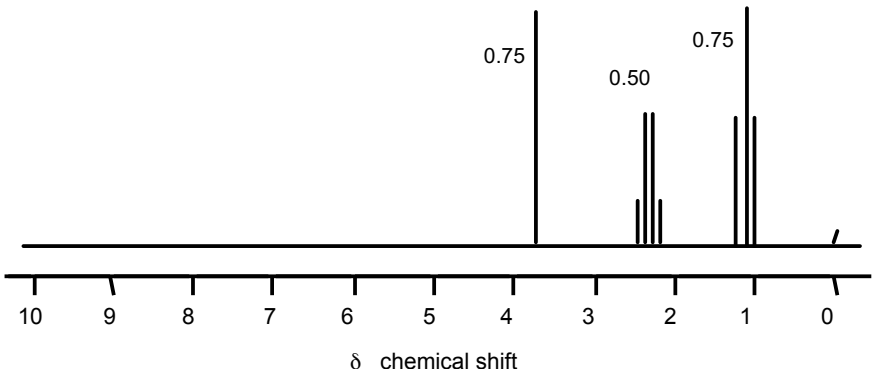
b) Indicate the number of signals, and relative intensity and multiplicity of each signal for each isomer.

c) Deduce which spectrum belongs to which isomer.

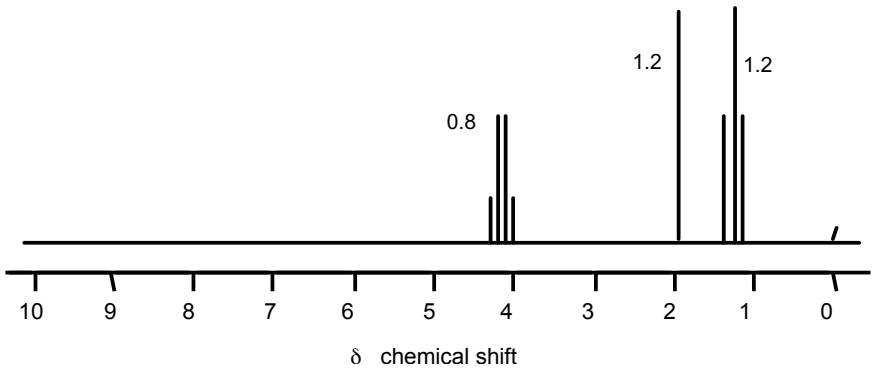
Spectrum I



Spectrum J

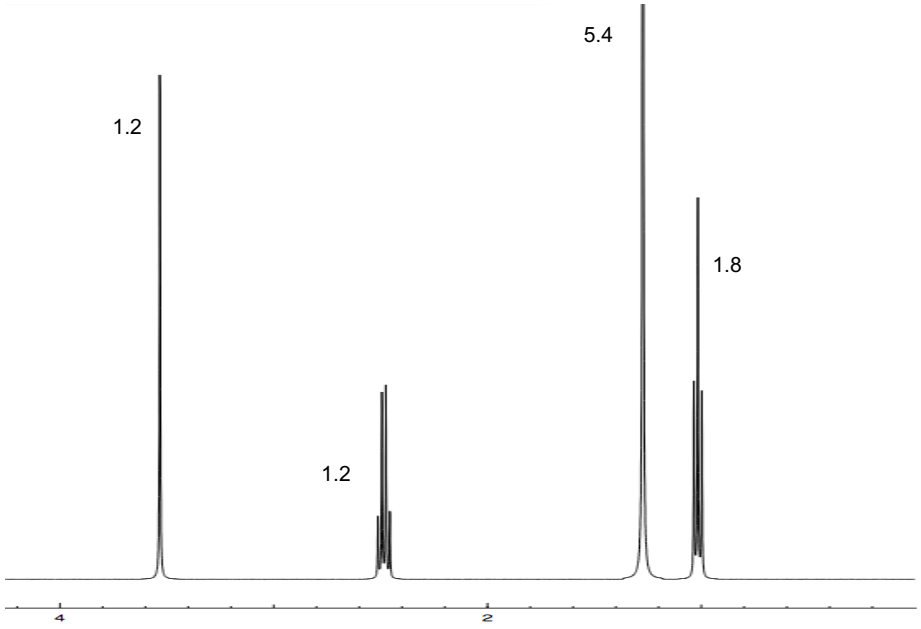


Spectrum K

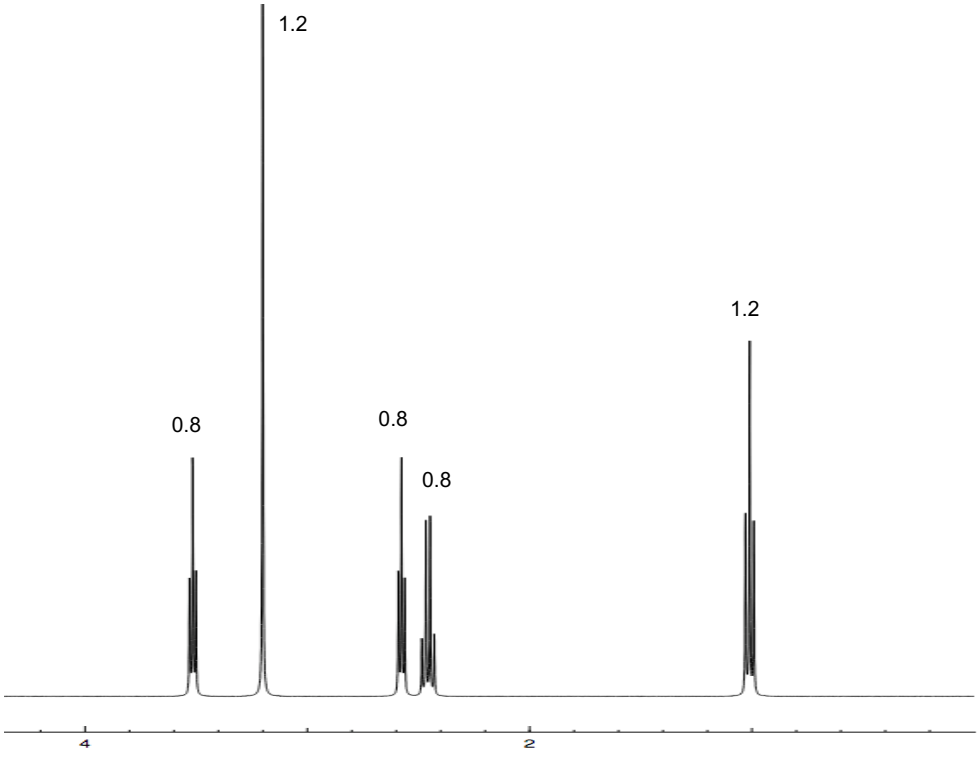


TASK 7 – Identifying compounds using ^{1}H NMR

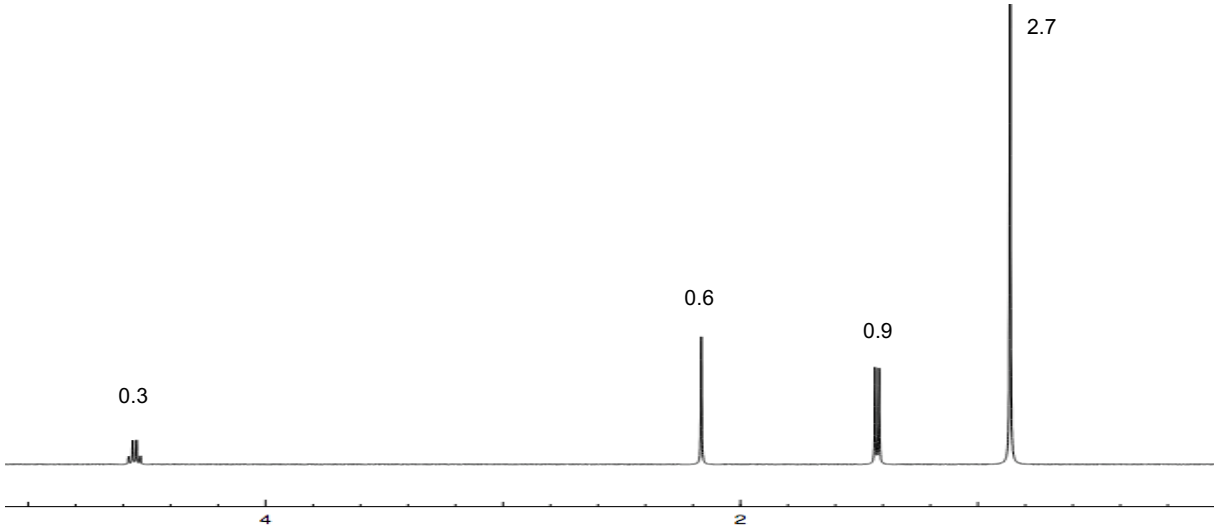
1 The ^{1}H NMR spectrum of $C_9H_{16}O_2$ is shown. The compound has a large peak at 1705 cm^{-1} in its IR spectrum. It does not react with sodium hydrogencarbonate or Tollen's reagent. Deduce the structure of the compound.



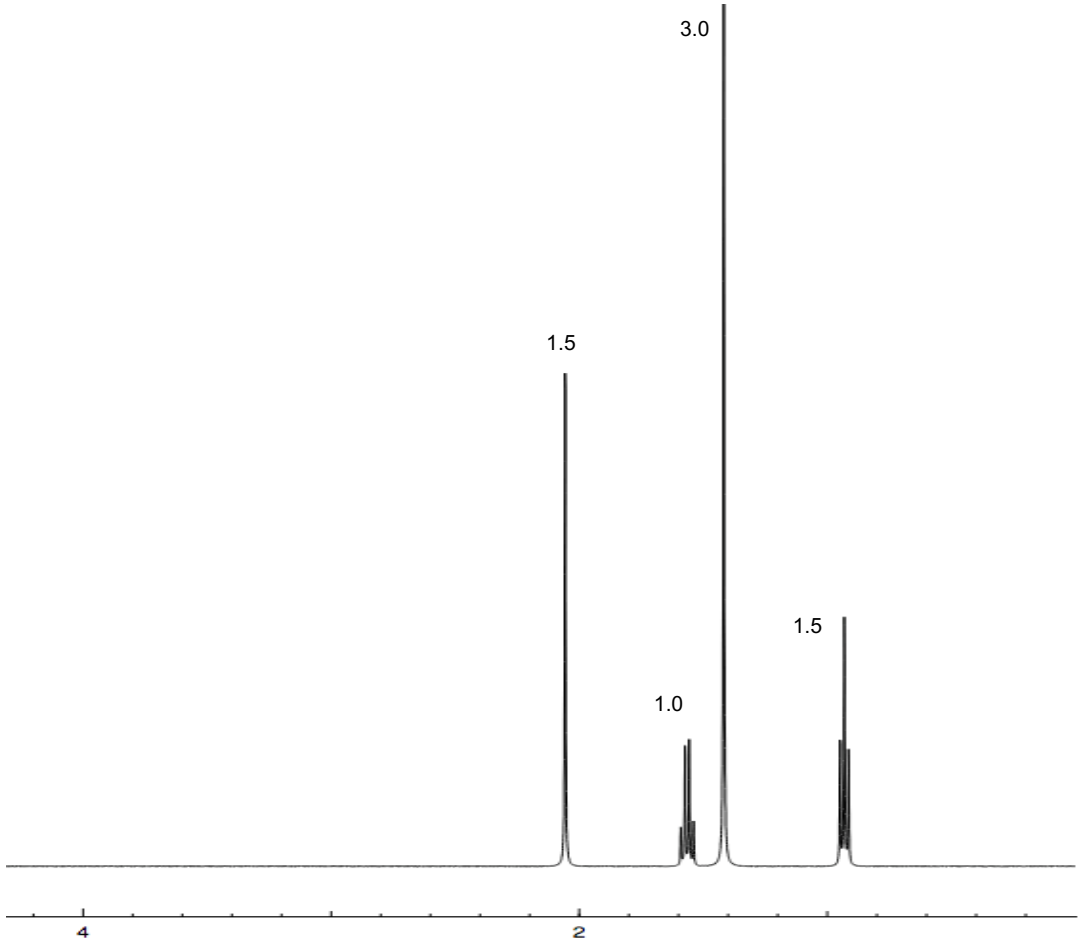
2 The ^{1}H NMR spectrum of $C_6H_{12}O_2$ is shown. Deduce the structure of the compound.



3 The ^1H NMR spectrum of $C_8H_{15}OCl$ is shown. Deduce the structure of the compound.



4 The ^1H NMR spectrum of $C_7H_{14}O_2$ is shown which is an ester. Deduce the structure of the compound.



SECTION 2 – ^{13}C NMR

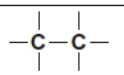
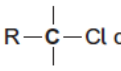
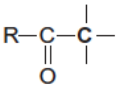
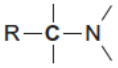
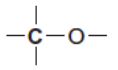
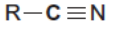
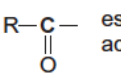
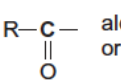
What is ^{13}C NMR?

- ^{13}C NMR is another powerful analysis technique for organic chemists.
- The spectrum is run in the same way and often on the same sample as the ^{1}H NMR spectrum dissolved in CCl_4 or a deuterated solvent such as $CDCl_3$. (note that there will also be signal(s) for the ^{13}C atom(s) in the solvent)
- The table shows some key similarities and differences between ^{1}H or ^{13}C NMR spectra.

	Similar or different	^{1}H NMR	^{13}C NMR
Number of signals	similar	One signal for each set of equivalent ^{1}H or ^{13}C atoms	
Position of signal	similar	The closer the atom to a very electronegative atom and/or double bond, the greater the chemical shift	
Relative size of signals	different	Relative area of signals related to relative number of ^{1}H atoms	**No link** between area of signal to number of ^{13}C atoms
Splitting of signals	different	Signal split by ^{1}H atoms on adjacent atom (into doublets, triplets, etc)	**No splitting**

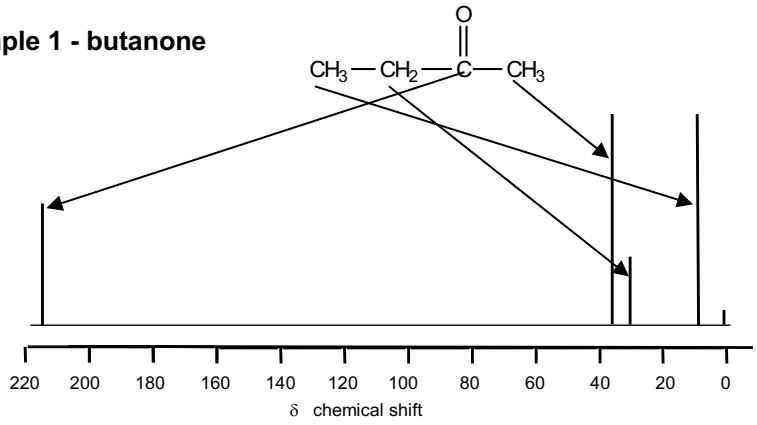
Chemical shift values

- The table shows some data for chemical shifts in ^{13}C NMR spectra.

Type of carbon	δ/ppm
	5 – 40
	10 – 70
	20 – 50
	25 – 60
 alcohols, ethers or esters	50 – 90
	90 – 150
	110 – 125
	110 – 160
 esters or acids	160 – 185
 aldehydes or ketones	190 – 220

Examples of ^{13}C NMR spectra

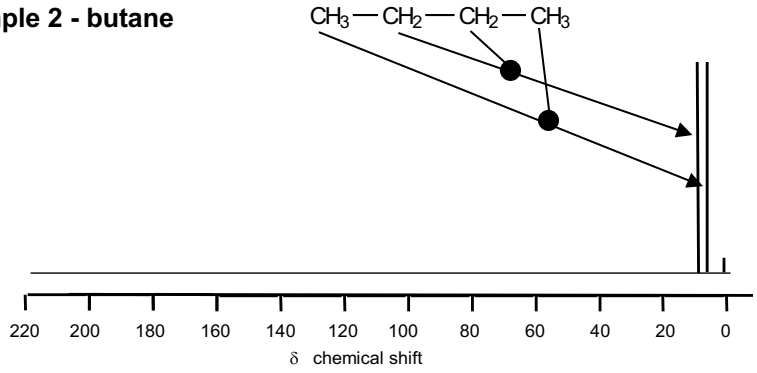
Example 1 - butanone



shift (δ)	assignment
8	$\underline{C}H_3CH_2$
32	$\underline{C}H_3CO$
37	CH_2
215	CO

- Note how the C of the C=O group directly next to the O has the biggest chemical shift.
- Note how the C furthest from the O has the smallest chemical shift.

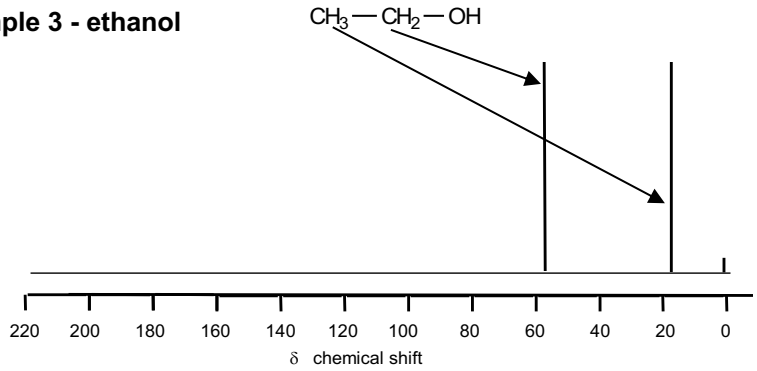
Example 2 - butane



shift (δ)	assignment
8	CH_3
10	CH_2

- There are only 2 signals as each signal represents 2 C atoms that are equivalent.
- You would not be expected to know which signal was for which C atom.

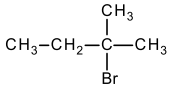
Example 3 - ethanol



shift (δ)	assignment
18	CH_3
58	CH_2

- Note how the C closest to the O has the biggest chemical shift.

TASK 8 – Predicting ^{13}C NMR spectra

Compound	Structure	Number of signals	Position of signals
2-bromo-2-methylbutane		4	δ 5-40 (**C**H_3CH_2), δ 5-40 (CH_3**C**H_2), δ 10-70 (CBr), δ 5-40 ((**C**H_3)$_2$CBr)
methylpropene			
propene			
2-chloropropane			
propanone			
methylamine			
ethyl propanoate			
1,2-dibromopropane			
dimethylethyl propanoate			
but-2-ene			

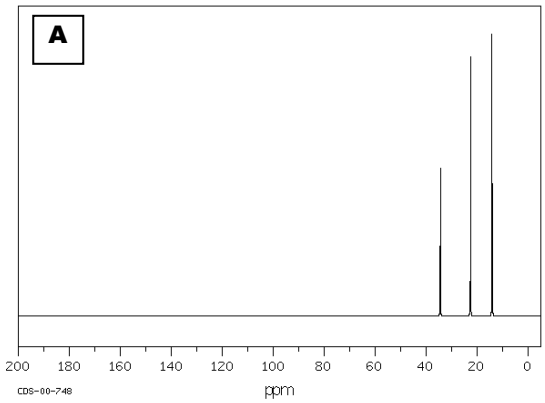
TASK 9 – Which ^{13}C NMR spectrum is which?

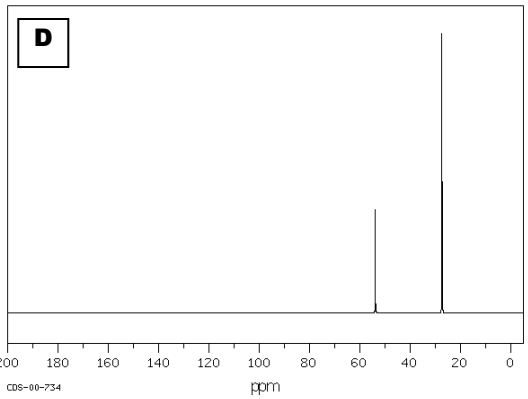
For each of the following compounds:

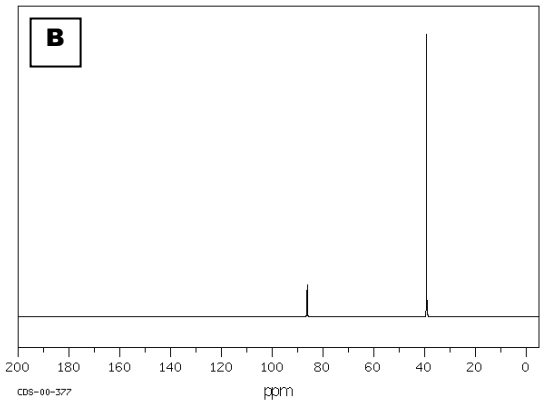
propanoic acid pentane 2-chlorpropane propanone 2,2-dichloropropane 2,3-dimethylbut-2-ene

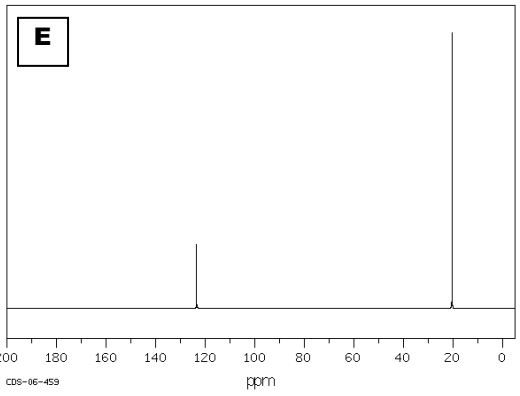
a) For each compound, predict the number of signals, and position of each signal.

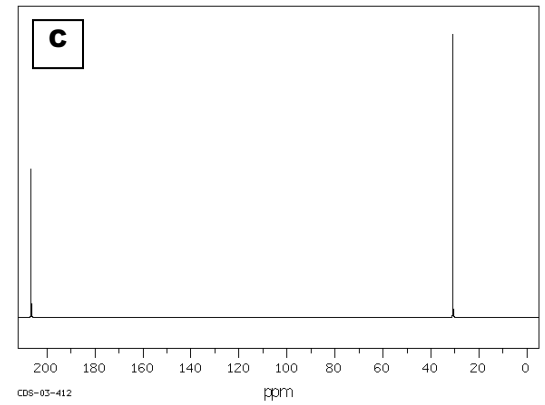
b) Work out which spectrum belongs to which compound.

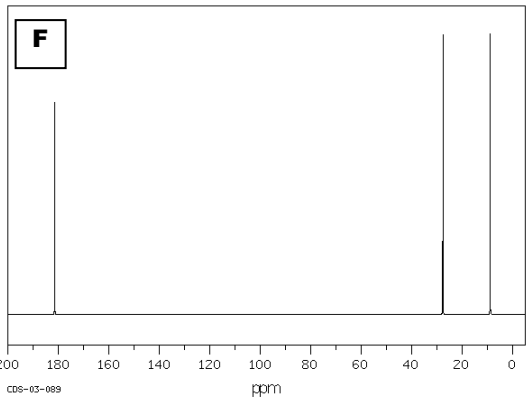






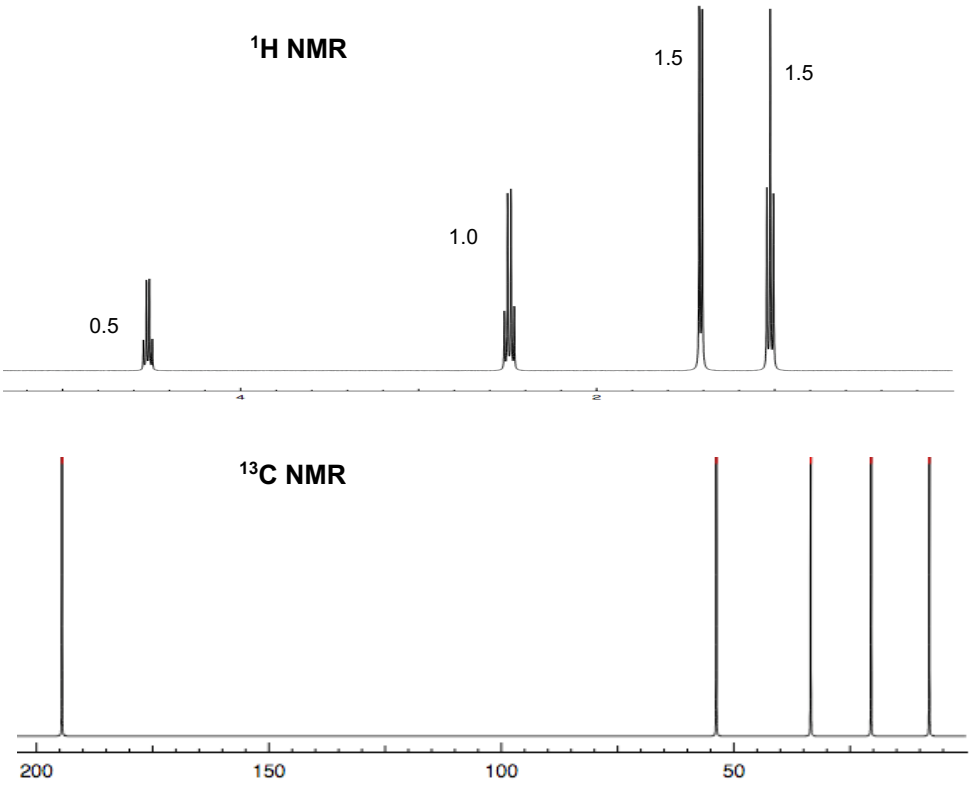




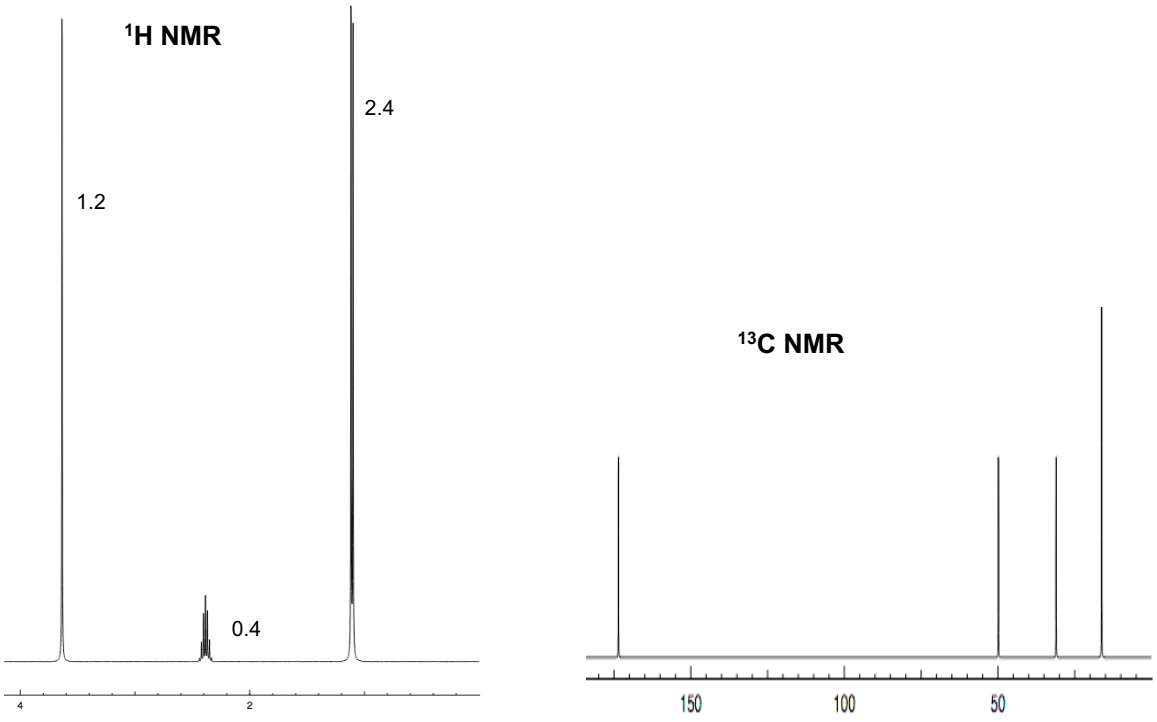


TASK 10 – Using ^{1}H and ^{13}C NMR together to identify compounds

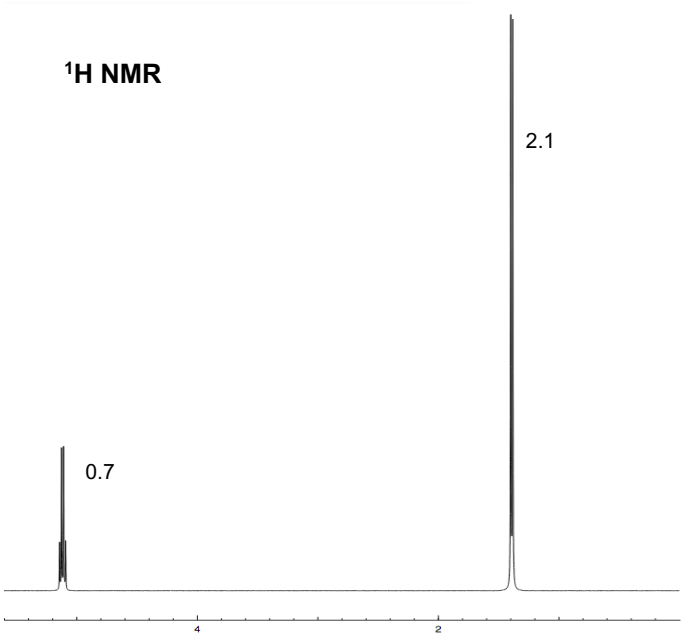
1 The ^{1}H and ^{13}C NMR spectra of C_5H_9OCl are shown Deduce the structure of the compound and then identify which signal represents which atom(s).

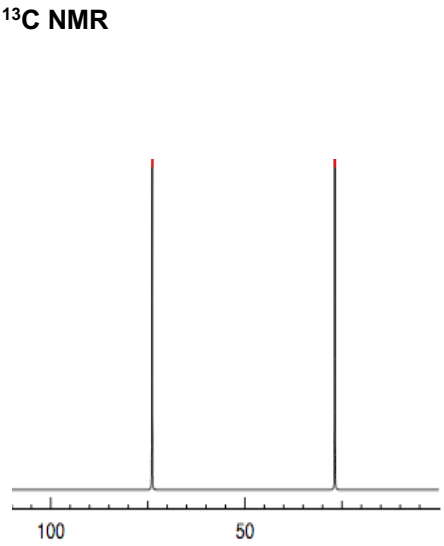


2 The ^{1}H and ^{13}C NMR spectra of $C_5H_{10}O_2$ are shown. Deduce the structure of the compound and then identify which signal represents which atom(s).



3 The ^{1}H and ^{13}C NMR spectra of $C_4H_8OBr_2$ are shown. Deduce the structure of the compound and then identify which signal represents which atom(s).





4 The ^{1}H and ^{13}C NMR spectra of $C_6H_{10}O_3$ are shown. Deduce the structure of the compound and then identify which signal represents which atom(s).